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The isopropylation of biphenyl over transition metal substituted aluminophosphates: MAPO-5 (M: Co and Ni)



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ABSTRACT

The isopropylation of biphenyl (BP) was examined over transition metal substituted aluminophosphates (MAPO-5; M: Co and Ni) with 12-membered (12-MR) oxygen ring pore-entrances of AFI topology. The MAPO-5 samples were synthesized by dry gel conversion method using trimethylamine as a structure directing agent, and their properties were characterized by XRD, XPS, SEM, N₂ adsorption, NH₃-TPD, pyridine adsorption, and o-xylene uptake. They are clear crystals without impurity phases and agglomerates, and found small amounts of Brønsted acid sites which are expecting active for acid catalysis. The isopropylation of BP over both of Co(5)APO-5 and Ni(5)APO-5 at 250 °C gave the high selectivities for 4,4'-DIPB: 65-75%. 4-IPBP is almost exclusive precursor of 4,4'- and 3,4'-DIPB. 3-IPBP was not significantly concerned even though 3-IPBP was predominant among IPBP isomers at the late stages: the MAPO-5 channels allow preferential access of 4-IPBP, and prevent the access of 3-IPBP due to reactant selectivity mechanism. The selective formation of 4.4'-DIPB occurred by preferential exclusion of bulkier 3.4'-DIPB and other isomers through the steric interaction of transition states with the channels by the restricted transition state selectivity mechanism. MAPO-5 (M: Co and Ni) has the same level of the selectivities for 4,4'-DIPB to SSZ-24 and other MAPO-5 (M: Si, Mg, and Zn), and these selectivities were originated by the AFI channels. The selectivities for 4,4'-DIPB were kept 65–75% at low and moderate temperatures over MAPO-5 (M: Co and Ni); however, they were decreased by the isomerization to stable 3,4'-DIPB with the increase in temperature.

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1. Introduction

Shape selective catalyses in confined environments of ordered solid acids introduce a type of controls for the prevention of bulky products in their channels, resulting in the formation of the least bulky products which are not always kinetically and/or thermody-namically favored [1,2]. Ordered molecular sieves, such as zeolites, are the most favorable candidates for the purpose because their pores and channels are uniformly distributed, and their dimensions

http://dx.doi.org/10.1016/j.molcata.2015.11.006 1381-1169/© 2015 Elsevier B.V. All rights reserved. allow both reactants and products to enter, reside, and leave in the catalytic process [1].

Shape-selective catalyses over zeolites are based on the differentiation of reactants, products, and/or reaction intermediates according to shape and size in sterically confined environments [3]. If the zeolite pores and channels are small enough to accommodate both of reactants and products, the reactant conversion and product formation probabilities are determined by the molecular sizes and the configurations of the pores and channels. Only a reactant molecule smaller than the critical sizes against the pores, can enter in the pores, and reacts at the catalytic site in the channels. Furthermore, only a product molecule, which can diffuse out through the pores, appears as a product. Therefore, it is important to fit zeolites with the type of catalysis. In particular, the shape-selective catalysis appears through interaction of zeolites with reactants, transition

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states, and products by "reactant", "product", and "restricted transition state" selectivities [3].

Ordered microporous aluminophosphates (APO) were first synthesized by Wilson et al. in 1982 [4]. They have frameworks composed of networks of aluminum and phosphorous with similar topologies of zeolites. They are expected to work as molecular sieves for the catalysis, separation of organic compounds, etc. The drawback of these materials as catalytic materials, particularly for acid catalysis, is low acidity because of neutral tetrahedral framework composed of aluminum (three valence) and phosphorous (five valence); however, the introduction of the other metal cations to their frameworks enhances the appearance of acidities: typical examples are silicoaluminophosphates (SAPO) and other metalloaluminophosphates (MAPO) by Flanigen and her co-workers [5,6]. The valent imbalance by partial replacement of Al³⁺ by divalent cations or P⁵⁺ by tetravalent cations gives rise to Brønsted acid sites [7]. The addition of metal cations will expand the number and diversity of the APO, and afford new properties to the microporous materials, such as acid catalysis, oxidation, etc. depending on the types of metal species [9,10].

The isopropylation of biphenyl (BP) is a typical acid catalysis in Friedel–Crafts alkylation of aromatic hydrocarbons, which demonstrates the shape-selective nature of the molecular sieve [10–21]. The selective formation of the least bulky 4,4'-diisopropylbiphenyl (4,4'-DIPB) should be facilitated over ordered microporous materials if the catalytic sites are properly restricted by their channels [10–12,13].

In the previous papers, we described that 4,4'-DIPB has been selectively produced from BP over dealuminated H-mordenite (MOR) [12,13]. We also found SSZ-24 with AFI topology has high potentials for the shape-selective formation of 4,4'-DIPB [14–16]. However, most of previous works on the alkylation of polynuclear hydrocarbons have used zeolites as catalysts, and there are only a few works using MAPO [18–21]. It is interesting to explore the possibilities of shape-selective catalysis by large pore MAPO. Among them, we focused on the MAPO-5 of AFI topology, which are isostructural with SSZ-24 [22]. We found MAPO-5 (M: Si, Mg, and Zn) for aluminophosphate version and SSZ-24 for aluminosilicate version gave the almost same levels of the selectivities for 4,4'-DIPB [14–16,18–20]. These results indicate that shape-selective natures of these materials are due to AFI topology based on their oxygen rings.

In this paper, we examined the isopropylation of BP over transition metal substituted APO-5 (MAPO-5; M: Co and Ni) in order to clarify the influence of transition metals in the acid catalysis. This is the first example succeeding in shape-selective catalysis for transition metal substituted APO-5.

2. Experimental

2.1. Reagents

Aluminum triisopropoxide, cobalt(II) acetate tetrahydrate (Co(OAc)₂·4H₂O), and nickel(II) acetate tetrahydrate (Ni(OAc)₂·4H₂O), and phosphoric acid (85%), trimethylamine (Et₃N), BP, and other organic chemicals were obtained from Sigma–Aldrich. 4,4'-Diisopropylbiphenyl (4,4'-DIPB) was purchased from Tokyo Chem. Ind., Tokyo, Japan.

2.2. The synthesis of MAPO-5 (M: Co and Ni)

The synthesis of CoAPO-5 was carried out by dry gel conversion method (vapor phase transfer method) [23]. The gel composition for the synthesis of Co(5)APO-5 was as follows: $1.0Al_2O_3-0.03-0.40CoO-1.0P_2O_5-0.76Et_3N-45H_2O$. The typical procedures are as

follows: 2.05 g of aluminum triisopropoxide (5.0 mmol as Al₂O₃) was slurred in water (1.85g). To this slurry, 1.15g of 85% phosphoric acid (5.0 mmol as P_2O_5) diluted in water (2.0 g) was added dropwise over a period of 0.5 h with constant magnetic stirring. To the resulting solution, a 0.107 g of cobalt acetate (0.5 mmol as CoO) was added and the stirring was further continued for 0.5 h. The gels thus obtained were dried at 80 °C in an oil bath with continuous magnetic stirring to remove water. When the gel became thick and viscous, it was homogenized manually using a Teflon rod and this was continued until it dried. The gels in Teflon cups were placed in the autoclaves (23 ml, Parr Instrument Co., IL, U.S.A.), and, finally, a mixture of 384 mg of Et₃N (3.8 mmol) and 150 mg of water was taken at the bottom so as to be supplied as water vapor. The crystallization was carried out by heating the autoclave statically at 175 °C for 24 h in a convection oven. The autoclave assembled for the synthesis is shown in our previous paper [22].

After the crystallization, the products were washed with distilled water, separated by centrifugation, and dried at $100 \,^{\circ}$ C overnight. The as-synthesized samples were calcined in a muffle furnace in a flow of air (flow rate: $50 \,\text{ml/min}$) as follows: the temperature was raised from room temperature to $550 \,^{\circ}$ C in 4 h, kept at this temperature for another 7 h, and finally cooled to room temperature in ambient conditions.

NiAPO-5 was synthesized in a similar manner to CoAPO-5 using nickel acetate as NiO precursor.

The resultant aluminophosphates are expressed as M(x)APO-5, where M is transition metals, and x is input percentage of substituted metal (mol) with aluminum (mol) (see Table 1).

2.3. The isopropylation of BP over MAPO-5 (M: Co and Ni)

The alkylation of BP was carried out in a 100-ml SUS-316 autoclave (Nitto Koatsu, Tsukuba, Japan) under a constant pressure of propene. Typical procedures of the isopropylation of BP are as follows: BP (3.84 g, 20 mmol) and Co(5)APO-5 (100 mg) were mixed in an autoclave, which was flushed with nitrogen followed by heating to a desired temperature. Propene was then introduced to the desired pressure (0.8 MPa), and the reaction started by the agitation. The pressure was maintained throughout the reaction period (4h). After the reaction, the autoclave was cooled, and the catalyst was filtered and washed with toluene (10 ml). The solution (ca. 1.5 ml) was taken from the total bulk products and diluted with toluene (1.5 ml). The products were identified by gas chromatography-mass spectroscopy on Shimadzu GC-MS; QP5000, and analyzed by a Shimadzu 2010plus gas chromatograph equipped with an Ultra-1 capillary column ($25 \text{ m} \times 0.2 \text{ mm}$; film thickness: 25 µm; Agilent Technologies).

The conversion of BP and the yield of each product were calculated on the basis of consumed BP. The selectivities for each DIPB and isopropylbiphenyl (IPBP) isomer are expressed based on total amounts of IPBP and DIPB isomers, respectively.

The products encapsulated in the catalysts were analyzed as follows: after collection of the bulk products (as mentioned earlier), the catalyst was washed 5 times with 20 ml of acetone, and dried at 110 °C for 12 h. Then 20 mg of resulting catalyst was carefully dissolved in 0.5 ml of concentrated hydrochloric acid (35%) at room temperature. This solution was basified with solid potassium carbonate, and the organic layer was extracted three times with 2 ml of dichloromethane. After removing of the solvent *in vacuo*, the residue was dissolved in 0.5 ml of toluene. GC analysis was performed similarly to the case of bulk products.

2.4. The characterization of MAPO-5 (M: Co and Ni)

Crystallinity and phase purity of MAPO-5 were confirmed on a Rigaku Ultima III X-ray diffractometer with Cu K α radiation

Table 1	
Syntheses of MAPO-5 (M: Co and Ni) and their textual properties	s.

	Input/molar ratio			Output/molar ratio		$BET/cm^2 g^{-1}$	<i>t</i> -plot/cm	² g ⁻¹	Pore volume/cm ³ g ⁻¹	
	M/P	Со	Al	Р	M/AI	(Al+Co)/P		Micro	External	
Co(3)APO-5	0.03	0.15	5.0	5.0	0.029	1.187	262	202	60	0.079
Co(5)APO-5	0.05	0.25	5.0	5.0	0.054	1.150	254	192	61	0.076
Co(10)APO-5	0.10	0.50	5.0	5.0	0.103	1.085	n.d.	n.d.	n.d.	n.d.
Co(20)APO-5	0.25	2.00	8.0	5.0	0.265	1.047	263	192	72	0.076
Co(30)APO-5	0.43	3.00	7.0	5.0	0.467	1.093	220	159	60	0.063
Co(40)APO-5	0.67	4.00	6.0	5.0	0.532	1.081	127	73	55	0.032
Ni(5)APO-5	0.05	0.25	5.0	5.0	0.057	1.159	189	43	145	0.025

 $(\lambda = 0.15418 \text{ nm})$. The bulk composition of MAPO-5 was determined by Bruker S8 Tiger X-ray Fluorescence Spectrometer. XPS spectra were recorded on MultiLab 2000 spectrometer (VG Systems, LLC, Co., VA, USA). The observation of morphologies was carried out using a Hitachi S-4700 Scanning Electron Microscope. N₂ adsorption isotherms were recorded on a Micromeritics 3Flex and Tristar 3020 Analyzers and/or a MireaSI nanoPorosity-XG Analyzer. Pyridine adsorption was recorded on a Shimadzu FT-IR spectrometer, IRTracer-100, with an MCT detector and a vacuum IR cell (Makuhari Rikagaku Garasu Inc., Chiba, Japan). IR spectra of adsorbed pyridine on wafer were obtained under the exposure of 0.75-5.5 Torr of pyridine by rapid scan during 60 s in every 0.19 s (resolution: 4 cm⁻¹) after the evacuation at 400 °C during 1 h. Finally, the spectra of pyridine strongly adsorbed were obtained after the evacuation for 30 min. under 0.5 Torr at room temperature. Uptakes of o-xylene on MAPO-5 were measured using a gravimetric adsorption system equipped with a quartz spring. The sample was first evacuated at 300 °C for 1 h, and the mass gain was measured at 90 °C during 30 min after exposing 6.1–6.7 Torr of o-xylene.

3. Results and discussion

3.1. The characterization of MAPO-5 (M: Co and Ni)

Fig. 1 shows XRD patterns of MAPO-5. All of them have the patterns of AFI topology. The distinct diffraction of AFI topology was observed in the wide range of cobalt content (3–30%). There were no patterns of impurities and agglomerated cobalt species even for Co(30)APO-5, either. Ni(5)APO-5 also had the patterns of AFI topology.

XPS observation suggests that cobalt and nickel were trivalent oxides in the materials (data not shown). These results mean metal species are in arrays of APO-5, where metal species were present as mixed phosphate clusters of cobalt and aluminum in the channels, and the isomorphously substituted M²⁺ species with Al³⁺ in the framework were not observed due to their small amounts as dicussed below. The formation of cobalt cluster in CoAPO-5 channels has been suggested by van Breukelen et al. [24].



Fig. 1. XRD patterns of MAPO-5 (M: Co and Ni).

Fig. 2 shows SEM images of MAPO-5 samples. They have wellordered plate type clear crystals. The crystal size of Co(5)APO-5 were smaller than APO-5 and Ni(5)APO-5. There are no agglomerates assigned to cobalt and nickel species.

Nitrogen adsorption isotherms of MAPO-5 are shown in Fig. 3. Amount of N_2 adsorbed in micropores are around 70 cm³/g (stp) for APO-5 and Co(5)APO-5; however, 30 cm³/g for Ni(5)APO-5. These differences indicate the Ni(5)APO-5 is lowly crystallized compared to APO-5 and Co(5)APO-5, although clear XRD patterns and SEM were observed as in Figs. 1 and 2. Table 1 shows that BET surface areas and pore volumes were decreased with the increase in cobalt contents of CoAPO-5. *t*-Plot calculation indicates that micropores are decreased with the increase in external surface areas by the increase of cobalt contents. These results suggest that the crystallinities were decreased with increase in cobalt content, and that



Fig. 2. SEM images of MAPO-5 (M: Co and Ni).



Fig. 3. N₂ adsorption isotherms of MAPO-5 (M: Co and Ni). Legend: ■: Co(5)APO-5;
 Ni(5)APO-5; A: APO-5.



Fig. 4. o-Xylene uptake on MAPO-5 (M: Co and Ni).

small particles of mixed aluminum and cobalt phosphate at extraframework of CoAPO-5 are choked the channels with the increase in cobalt content.

Uptakes of *o*-xylene on MAPO-5 are shown in Fig. 4. *o*-Xylene can easily enter and accommodate in MAPO-5 channels. All MAPO-5 rapidly uptake *o*-xylene within 3 min, and then, uptakes are slowed down. The amounts after 20 min are in the order: Ni(5)APO- $5 \ll CoAPO-5 \le APO-5$. The results also indicate that APO-5 and Co(5)APO-5 have well-ordered microporous channels in them, and that Ni(5)APO-5 has less crystallinity with low pore volume.

NH₃-TPD profiles of MAPO-5 are shown in Fig. 5. Co(5)APO-5 and Ni(5)APO-5 have three types of peak, although there were only weak peaks on APO-5. The deconvolution of peaks suggests that they have three major peaks at 200, 380, and 440 °C. Peaks at around 200 °C are assigned to physically adsorbed NH₃ and peaks around 380 °C are assigned to strong acid sites expecting active for the acid catalysis. The wide peaks at around 440°C are also assigned the desorbed NH₃ from strong acid sites. It is possible that 2nd and 3rd peaks involve Brønsted (B-) and Lewis (L-) acid sites [25,26]. To know the type of acidities, we examine the observation of adsorbed pyridine on MAPO-5 by IR spectroscopy. Fig. 6 shows the pyridine adsorption on MAPO-5, where excess of pyridine was evacuated at 0.5 Torr for 30 min at room temperature. All MAPO-5 samples have small peaks assigned to pyridine adsorbed on B-acid sites at 1540 cm⁻¹, and another absorption around 1444 cm⁻¹ assigned to pyridines adsorbed on Lewis acid (L-acid) sites [27]. Unexpectedly, these results suggest that the B-acid sites, appeared on MAPO-5 by



Fig. 6. IR spectra of pyridine adsorbed on MAPO-5 (M: Co and Ni).

the isomorphous substitution of M^{2+} with Al^{3+} in the frameworks of APO-5 [7–9], are only in small amounts, probably due to difficulty of substitution of large Co²⁺ cation with Al^{3+} in the frameworks. However, we consider that they are enough for the acid catalysis, such as Friedel–Crafts alkylation. There are the examples of high activities with very small amounts of B-acid sites in the isopropylation of BP over highly dealuminated MOR [13,17]. The large amounts of L-acid sites are considered to exist probably on mixed metal and aluminum phosphate at extra-framework of APO-5 channels; however, further studies are necessary on the natures of the phosphate and L-acid sites on them.

The input and output results of the synthesis of MAPO-5 are shown in Table 1. Molar ratios of (Al + Co)/P were remained around 1.0–1.2. These results mean that the materials obtained by our synthesis are substituted APO-5, and that each components were well balanced after the synthesis.

From the results, cobalt and nickel species are considered to exist either as the isomorphously substituted M²⁺ with Al³⁺ in the framework of APO-5, or as mixed metal and aluminum phosphates in extra-framework of the channels because all MAPO-5 have similar XRD patterns with no particular large agglomerates, and the surface area and pore volume from nitrogen isotherm were gradually decreased with the increase in cobalt content. However, we have no information of the properties of the mixed phosphates in



Fig. 7. The isopropylation of BP over CoAPO-5 (Co: 5-40). Reaction conditions: BP: 20 mmol; CoAPO-5: 100 mg; temperature: 250 °C; propene pressure: 0.8 MPa; period: 4h. Legend: : 4,4'-DIPB; : 3,4'-DIPB; : 3,3'-DIPB; : 2,x'-DIPB; : 3,4'-DIPB; : 3,4'-D

MAPO-5 channels. Further investigations are necessary for understanding their details of the metal species in the channels.

3.2. The isopropylation of BP over MAPO-5 (M: Co & Ni)

3.2.1. The isopropylation over CoAPO-5

Fig. 7 shows the effects of cobalt content of CoAPO-5 on the isopropylation of BP. Catalytic activities were not found for AlPO-5 [19]: they appeared by the introduction of cobalt species. They were the highest at 3–5% of cobalt content; however, decreased with further increases in cobalt content. The decreases are due to the decrease in surface area by choking mixed cobalt and aluminum phosphate in microporous APO-5 channels as suggested in previous section. The selectivities for the least bulky 4,4'-DIPB were around 70% among DIPB isomers, and the combined selectivities for 4,4'-DIPB and the secondly least bulky 3,4'-DIPB were over 95%: the channels of MAPO-5 were highly shape-selective for the least bulky 4,4'-DIPB and the second least bulky 3,4'-DIPB among DIPB isomers. These selectivities are almost in the same level as SSZ-24 and MAPO-5 (M: Si, Mg, Ca, Sr, Ba, Zn) with AFI topology [14–16,18–20].

3.2.2. Reaction profiles of the isopropylation of BP

Typical reaction profile of the isopropylation of BP over Co(5)APO-5 under 250 °C and 0.8 MPa of propene pressure is summarized in Fig. 8. Fig. 8a shows the yields of IPBP and DIPB isomers over Co(5)APO-5. 4-IPBP appeared rapidly at low conversion of BP, saturated at 40–60%, and then, decreased with further increase in the conversion. 3-IPBP was minor among the isomers at low conversion. However, 3-IPBP was spontaneously accumulated with progress of the reaction because 4-IPBP was chosen as the preferential precursor of DIPB isomers even in the presence of large amounts of 3-IPBP. Further, 2-IPBP, the bulkiest isomer, was also spontaneously increased although the yield was less than 3%. The yields of 4,4'- and 3,4'-DIPB were increased with the conversion by accompanying preferential formation of the least bulky 4,4'-DIPB and the second least bulky 3,4'-DIPB among DIPB isomers.

Fig. 8b shows the selectivities for IPBP isomers during the isopropylation. 4-IPBP were predominant over 3-IPBP in the ratio of around 2 at the early stages. The selectivities for 4-IPBP, the least bulky isomers, were decreased with the increase of the conversion, accompanying concurrent increase in the selectivities for 3-IPBP. These changes correspond well to the yields of IPBP isomers as shown in Fig. 8a. Further, the selectivities for 4-IPBP in encapsulated products were remained almost constant at around 70% during the reaction. These results indicate that 4-IPBP was consumed steadily for the formation of 4,4'- and 3,4'-DIPB in the channels, and that 3-IPBP was not concerned on the formation of 3,4'-DIPB during the reaction even though 3-IPBP was predominant among IPBP isomers at the late stages.

The selectivities for DIPB isomers are shown in Fig. 8c. The selectivities for the least bulky 4,4'-DIPB in bulk products were around 70%; and were slightly decreased to 60% at the late stages. The selectivities for the second least bulky 3,4'- DIPB were 30–35% throughout the isopropylation. The selectivities for 4,4'-DIPB in encapsulated products were remained almost constant and in the same levels as in bulk products as in Fig. 8c. These results show that shape-selective formation of the least bulky 4,4'-DIPB occurred from 4-IPBP by the preferential exclusion of the bulkier 3,4'-DIPB in CoAPO-5 channels.

The isopropylation of BP over Ni(5)APO-5 was examined to compare the results of Co(5)APO-5 (Fig. 9). The profiles were quite similar to each other's: 4-IPBP is almost exclusive precursor of 4,4'and 3,4'-DIPB during the reaction. NiAPO-5 channels allow preferential access of 4-IPBP, and prevent the access of 3-IPBP in spite of predominance of 3-IPBP at the late stages. The selectivities for 4-IPBP and 4,4'-DIPB in encapsulated products also indicate that the isopropylation occurs in the NiAPO channels as discussed for Co(5)APo-5.

These results suggest that the catalyses over the MAPO-5 (M: Co and Ni) occur at the internal B-acid sites in resembled circumstances in their channels with AFI topology, and that these metals work as active sites for the acid catalysis. The substitution with transition metals gave no significant influence for the formation of by-products at such a moderate temperature as $250 \,^{\circ}C$ (Figs. 8 and 9).

3.2.3. The isomerization of 4,4'-DIPB during the isopropylation of BP

Figs. 10 shows the effects of reaction temperature on the selectivity of DIPB isomers in the isopropylation of BP over Co(5)APO-5 under 0.8 MPa of propene pressure. The selectivities for 4,4'-DIPB in bulk products were as high as 70% at low and moderate temperatures; however, they were gradually decreased with the increase in the temperatures from around 250–275 °C, and then, rapidly with further increases up to 350 °C. The decrease in the selectivities for 4,4'-DIPB. The selectivities for 3,3'-DIPB were gradually increased with the increase in the temperature; however, remained in the levels of 10% even at 350 °C. Equilibrium composition of DIPB isomers at 300 °C: 3,4'-33%, 3,3'-37%, 4,4'-9%, 3,5–17%, and others 4% [28]. These values suggest 4,4'-DIPB rapidly isomerizes to 3,4'-DIPB; however, further isomerization to equilibrium composition takes long time at 270–350 °C.

The selectivities for 4,4'-DIPB in encapsulated products were remained in the similar levels as those in bulk products up to 275 °C. However, we could not obtain the clear results of the selectivities for DIPB isomers in encapsulated products at higher temperatures due to disturbance of unidentified components in GC analysis formed during the reaction and/or during working up.

Fig. 11 shows the effects of reaction temperature on the selectivities for DIPB isomers in the isopropylation over Ni(5)APO-5 under 0.8 MPa of propene pressure. The selectivities for 4.4'-DIPB in bulk products were remained at around 70% up to 300 °C, and the increase in the temperature accompanied the decrease in the selectivities for 3.4'-DIPB by the isomerization of 4.4'-DIPB.

The selectivities for 4,4'-DIPB in encapsulated over Ni(5)APO-5 were remained high in the level of 80% even with the increase in the temperature. These results mean the isomerization of 4,4'-DIPB occurred at the external acid sites, not in the channels of Ni(5)APO-5.



Fig. 8. Profiles of the isopropylation of BP over Co(5)APO-5. Reaction conditions: BP: 20 mmol; Co(5)APO-5: 100 mg; temperature: 250 °C; propene pressure: 0.8 MPa; period: 0.025-4 h.

3.3. Mechanistic aspects of the isopropylation of BP over MAPO-5

MAPO-5: CoAPO-5 and NiAPO-5 with transition metal substitution have AFI topology with straight channels of 12-MR pore entrances [4–9,22]. They are active for acid catalysis in Friedel–Crafts alkylation of aromatic hydrocarbons such as the isopropylation of BP. The activities are due to the B-acid sites, which appear by the isomorphous substitution of M²⁺ with Al³⁺ in the neutral frameworks of APO-5 [7–9]. There have been some examples of high activities by small amounts of acid sites over highly dealuminated MOR in the isopropylation of BP [13,17]. The other types of acid sites observed in large amounts are L-acid sites due to mixed metal and aluminum phosphate clusters at extra-frmaework in the channels. It is possible the latter types of L-acid sites have the activities for the solid catalysis; however, we consider that they are not principal for the isopropylation of BP.

The profiles of the isopropylation of BP gave us the interesting features in the catalysis in the AFI channels of MAPO-5. The isopropylation of BP occurred in the MAPO-5 channels by two consecutive steps at moderate temperatures as 250 °C. BP gave 4and 3-IPBP in the ratio of around 2 (obtained in the early stage); however, 2-IPBP was formed less than 3%. The channels allow predominant formation of both of 4- and 3-IPBP by restricted transition state selectivity mechanism. In the second step from IPBP to DIPB isomers, 4-IPBP was chosen as a precursor, and bulkier 3-IPBP was not much concerned the formation of DIPB isomers in spite of its predominance among IPBP isomers at the late stages. The selection of 4-IPBP against 3-IPBP occurred through reactant selectivity mechanism. Resultantly, 4-IPBP formed DIPB isomers with preferential formation of 4,4'-DIPB through the least bulky transition state compared to the second least bulky 3,4'-DIPB by the steric interaction with the channels through restricted transition state selectivity. These synergies of two mechanisms enhance the selectivities for 4,4'-DIPB in the second step from IPBP isomers to DIPB isomers as proposed in previous papers [10,11,13].

It is interesting in discrepancy between bulk and encapsulated products in the selectivities for IPBP isomers: the selectivities for 4-IPBP were around 80% in encapsulated products; however, 3-IPBP was predominant over 4-IPBP in bulk products. These results also mean that 4-IPBP can preferentially access to the channels and play the role in the precursor to DIPB isomers, irrespective of the amounts of 3-IPBP in the bulk products, because of the differences in bulkiness of two isomers. These results also support that the roles of 3-IPBP were very limited in the formation of 3,4'-DIPB in spite of predominance of 3-IPBP at the late stage. The similar profile was observed in the isopropylation of BP over MOR [10,11,13].

The high selectivities for 4,4'-DIPB over Co(5)APO-5 and Ni(5)APO-5 at low and moderate temperatures well correspond to the previous results that the microporous molecular sieves with AFI topology, SSZ-24 and MAPO-5 (M: Si, Mg, Ca, Sr, Ba, Zn) are active for the shape-selective formation of 4,4'-DIPB with the almost same level of the selectivities [18–20]. These results support our proposal that oxygen 12-membered rings of AFI topology afford the same level of shape-selective natures for the isopropylation, by the synergy of reactant and restricted transition state selectivities mechanisms [10,11,13].

The effects of reaction temperature suggest another feature of the isopropylation of BP over MAPO-5. The high selectivities for 4,4'-DIPB in bulk and encapsulated products at lower temperatures, such as $250 \degree C$, indicate the shape-selective natures of MAPO-5



Fig. 9. Profiles of the isopropylation of BP over Ni(5)APO-5. Reaction conditions: BP: 20 mmol; Ni(5)APO-5: 100 mg; temperature: 250 °C; propene pressure: 0.8 MPa; period: 0.05–8 h.



Fig. 10. The effects of temperature on the selectivity for 4,4'-DIPB in the isopropylation of BP over Co(5)APO-5. Reaction conditions: BP: 20 mmol; Co(5)APO-5: 100 mg; temperature: 200–350 °C; propene pressure: 0.8 MPa; period: 4 h.

channels: the formation of 4,4'-DIPB occurred from 4-IPBP through the preferential exclusion of bulky transition states by the channels, and the roles of 3-IPBP was very limited in the formation of 3,4'-DIPB due to product selectivity as discussed in previous section.

The decrease in the selectivities for 4,4'-DIPB occurred with the increase in temperature starting from 250 °C for Co(5)APO-5 and 300 °C for Ni(5)APO-5. The decrease in the selectivities for 4,4'-DIPB with concurrent increase in the selectivities for 3,4'-DIPB by the isomerization to 3,4'-DIPB directed towards the thermodynamic



Fig. 11. The effects of temperature on the selectivity for 4.4'-DIPB in the isopropylation of BP over Ni(5)APO-5. Reaction conditions: BP: 20 mmol; Ni(5)APO-5: 100 mg; temperature: 200–350 °C; propene pressure: 0.8 MPa; period: 4 h.

equilibrium. Judging from the selectivities for 4,4'-DIPB in encapsulated products over Ni(5)APO-5, 4,4'-DIPB was formed inside the channels, and isomerized to 3,4'-DIPB at the external acid sites; not inside the channels. Further isomerization of 3,4'-DIPB to 3,3'-DIPB was not observed at high temperatures, even at 350 °C in the isopropylation of BP over Ni(5)APO-5. However, we cannot discuss where the isomerization of 4,4'-DIPB occurs over Co(5)APO-5 because of lack of the information on encapsulated products.

The selectivities for 4,4'-DIPB in the bulk products were decreased with the increase in reaction temperatures in the iso-

propylation of BP over all materials with AFI topology, including SSZ-24 and MAPO-5 (M: Si, Mg, Zn, Co, and Ni), and their decrease in the selectivities for 4,4'-DIPB accompanied by the increase in those for 3,4'-DIPB by the isomerization towards thermodynamic equilibrium [14–16,18–20]. However, there are differences among the materials where the isomerization of 4,4'-DIPB occurred at the external and/or internal acid sites judging from the selectivities for 4,4'-DIPB in encapsulated products. The selectivities for 4,4'-DIPB in encapsulated products were decreased with temperatures over SSZ-24 and MAPO-5 (M: Si, Mg and Zn) [14–16,18–20]. These results indicate that the channels of AFI topology allow the accommodation of bulkier 3,4'-DIPB, resulting in the isomerization at internal acid sites as well as at external acid sites.

The isomerization of 4,4'-DIPB over Ni(5)APO-5 occurred only at external acid sites, and not at internal acid sites judging from the selectivities for 4,4'-DIPB in encapsulated products. This is quite different from other materials with AFI topology [14–16,18–20]. Currently, we cannot understand why cobalt and nickel promote the difference in the catalysis from the other materials. We expect further investigation of the properties of these materials will give the reasons of the differences.

The characterization of Ni(5)APO-5 indicates its low capacity of the channels; however, catalytic results are quite similar to Co(5)APO-5. This result means that AFI channels of Ni(5)APO-5 are very effectively worked in the isopropylation of BP.

4. Conclusion

Transition metal substituted aluminophosphates (MAPO-5; M: Co and Ni) with AFI topology were applied for the isopropylation of BP. They were synthesized by dry gel conversion method using trimethylamine as structure directing agent, and characterized by XRD, XPS, SEM, N₂ adsorption, NH₃-TPD, pyridine adsorption and *o*xylene uptake. They are clear crystals without impurity phases and agglomerates of metal species from XRD and SEM observations. N₂ adsorption and *o*-xylene uptake indicate that amounts of N₂ and *o*-xylene adsorbed on Ni(5)APO-5 were smaller than those on Co(5)APO-5. Pyridine adsorption suggests that both of the materials have only small amounts of B-acid sites in addition to large amounts of L-acid sites, where B-acid sites are active for the Friedel–Crafts alkylation.

Both of Co(5)APO-5 and Ni(5)APO-5 gave the high selectivities for 4,4'-DIPB: 65–75% in both of bulk and encapsulated products in the isopropylation of BP. 4-IPBP is almost exclusive precursor of 3,4'- and 4,4'-DIPB, and 3-IPBP was not significantly concerned in spite of its predominance among IPBP isomers at the late stages. The channels of the MAPO-5 allow preferential access of 4-IPBP, and prevent the access of 3-IPBP due to reactant selectivity mechanism. The selective formation of 4,4'-DIPB occurred by preferential exclusion of the second least bulky 3,4'-DIPB at the transition states through the steric interaction of transition states against the AFI channels by the restricted transition state selectivity mechanism.

The selectivities for 4,4'-DIPB were kept 65–75% at low and moderate temperatures over both of Co(5)APO-5 and Ni(5)APO-5, and they were decreased with the increase in temperature by the isomerization to 3,4'-DIPB towards thermodynamic equilibrium. The selectivities for 4,4'-DIPB in encapsulated products were almost constant over Ni(5)APO-5, irrespective of temperatures: the isomerization of 4,4'-DIPB occurred at the external acid sites, and not at the internal acid sites of Ni(5)APO-5. However, we cannot get the information of encapsulated products in Co(5)APO-5 at higher temepratures the isomerization occurred, due to the disturbance of unidentified components in GC analysis formed during the reaction and/or during working up formed during the reaction and/or during work-up. From the results, MAPO-5 (M: Co and Ni) have the same level of the selectivities for 4,4'-DIPB to SSZ-24 and MAPO-5 (M: Si, Mg, and Zn), and these selectivities were decided by AFI channels of 12-membered oxygen ring pore-entrances.

We found the small particles of the mixed metal and aluminum phosphate in the APO-5 channels. They may have high potentials for advanced materials, such as super capacitors, *etc.* Further studies on the aspects are under progress.

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